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SAMPLING AND ANALYSIS OF EBR-II SODIUM

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by

W. H. Olson

EBR-II Project

May 1971

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ABSTRACT

EBR-II sodium is sampled by two methods: overflow sampling and flow-through sampling. In overflow sampling, sodium from a spigot flows into and over the sides of a sample cup. In flow-through sampling, sodium flows directly through the sample vessel (a section of tubing or other container). In both methods, excess sodium used in flushing the sample vessel is returned to the system being sampled. Samples for radionuclide and trace-metal analyses are taken by the overflow method. Samples for oxygen, carbon, and hydrogen analyses are taken by the flow-through method. Principal radionuclides and their typical concentrations in EBR-II primary sodium are: ^{24}Na, 1400 $\mu Ci/g$; ^{22}Na, 5.0 x 10^{-2} $\mu Ci/g$; ^{137}Cs, 1.2 x 10^{-2} $\mu Ci/g$; and ^{131}I, 3.0 x 10^{-4} $\mu Ci/g$. Other radionuclides identified are ^{3}H, ^{117m}Sn, ^{113}Sn, ^{125}Sb, ^{110m}Ag, and ^{54}Mn. Principal metallic impurities and their typical concentrations in primary sodium are: Sn, 20 ppm; Pb, 10 ppm; and Bi, 2 ppm. Other metals of interest are all present in concentrations of <1 ppm. The only radionuclide in secondary sodium is ^{24}Na, 4.0 x 10^{-2} $\mu Ci/g$. Metals of interest in secondary sodium are all present in concentrations of <1 ppm. Carbon and oxygen in both sodium systems are present in concentrations of <2 ppm, hydrogen <0.1 ppm.

I. INTRODUCTION

Extensive revisions have been made in EBR-II sodium-sampling systems and methods and in sodium-analysis methods over the past four years (1967-1971). During the preceding period (1961-1967), sampling and analysis of EBR-II sodium were hampered by deficiencies in the state of the art and by fiscal limitations in development of equipment and methods. Table I summarizes significant events during that period.

Added impetus for an extensive program to characterize and monitor the quality of the sodium coolant of EBR-II was provided in 1967 following the discovery of copper in the primary sodium. A plugging indicator was removed from the primary-sodium purification system to investigate the

cause of a flow restriction. A copper plug was discovered in the valve of the indicator, and the internal surfaces of the heat economizer and cold-end lines were plated with copper. The reactor was shut down for two months while the source of copper was located and eliminated. An extensive sampling program then was carried out to determine the degree of copper contamination in EBR-II sodium, and studies were conducted to determine the effects of copper on sodium-contacted materials in EBR-II (principally Type 304 stainless steel) and to determine the solubility of copper in sodium.

TABLE I. Chronological Summary of Events Related to EBR-II Sodium Sampling and Analysis: 1961-1967

Date	Event
August 1961-February 1962	Formulation of sampling and analysis schedules intended for implementation during plant startup and early operation.
January 1963	Secondary system filled.
February 1963	Primary tank filled.
September 1963	Sampling and analysis schedules revised and abridged on basis of experience during early operation.
September 1964	Distillation method for oxygen deleted from sampling and analysis schedules. Revised schedules issued, including radiometric analyses for fission-product gases in primary argon.
July 1965	Status report on sodium sampling and analysis noted that no reliable technique was available for carbon analysis.
November 1965	Status report on sodium sampling and analysis recommended an expanded and aggressive program in collaboration with RE, CEN, and MET Divisions of ANL.
January 1966	Recommendation for strong sodium-chemistry program, especially to support experimental-irradiations program.
February 1966	Needs and recommendations for sodium-chemistry program restated.
April 1966	ANL proposed to RDT an expanded ANL sodium-technology program, including EBR-II support needs.
May 1966	Need for strong sodium-chemistry program reiterated with regard to EBR-II program plan and irradiations mission.
December 1966	Summary of the state of sodium analytical work for EBR-II, noting in particular that until summer 1966 no reliable method for carbon in sodium had been available.
February-June 1967	EBR-II "Copper Problem" investigations, plant and laboratory, in cooperation with MET Division and others.

The original EBR-II primary-sodium sampling system used a vacuum-distillation sampler.[1] Samples of the primary sodium, either upstream or downstream from the primary cold trap, could be taken for analysis. The residue left in the sampler after distillation was analyzed for sodium. The sodium was assumed to be Na_2O, and results were therefore reported as ppm oxygen in sodium. Results from these analyses were erratic and inconsistent, and the method was eventually abandoned.

Following the discovery of copper in the primary sodium in 1967, the sampling system was rebuilt and modified several times. Then, in 1968, the primary-sodium cold trap was replaced, and the entire purification and sampling systems were rebuilt.

Originally, the EBR-II secondary-sodium system contained no sampling system. However, a sampling system was installed in 1967. It is essentially the one in use today.

With existing sampling systems, samples may be taken by two methods. One, termed "overflow" sampling, consists of filling beakers or crucibles in an inert-atmosphere chamber. Sodium flows into and over the side of the beaker, and the overflow sodium returns to the system from a reservoir below the beaker. The other method, termed "flow-through" sampling, consists of filling sections of tubing or other vessels directly in-line. Sufficient sodium is flowed through the sample vessel to ensure that the sample is representative of system sodium.

The total sample taken by the overflow method is analyzed, but only a section of the sample taken by the flow-through method is analyzed. Therefore, in the latter sample, segregation of impurities could contribute to analytical error. However, preventing contamination of overflow samples by normal atmospheric contaminants is extremely difficult. For this reason, samples for oxygen, hydrogen, and carbon analysis are frozen in tubing or special vessels by the flow-through method, and sodium is then extruded as required for analysis.

Detailed analytical procedures are not described in this report. Methods currently used to analyze EBR-II sodium are described in detail in Ref. 2.

II. DESCRIPTION OF EBR-II SAMPLING SYSTEMS

A. Systems for Sampling Primary Sodium

Two systems carry primary sodium external to the primary tank: the primary-sodium purification system and the fuel-element-rupture-detection (FERD) loop. Sampling equipment is connected to both of these systems to facilitate removal of small quantities of sodium for chemical analysis.

Figure 1 is a schematic diagram of the primary-sodium purification system and its sampling system. Sodium is supplied from approximately midlevel in the primary sodium tank and returns to the tank above the sodium surface. The system is filled by drawing a partial vacuum on the surge tank. Flow is maintained with an electromagnetic pump. Sodium may be directed through the cold trap or through a bypass. A plugging indicator operates in parallel with the cold trap. Flow through the indicator is maintained by the pressure differential across the trap.

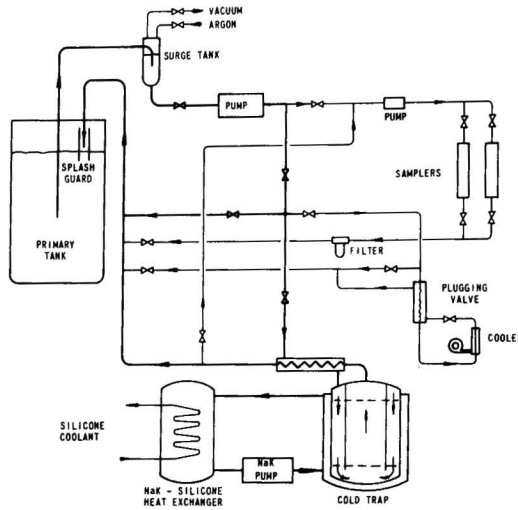

Fig. 1. Primary-sodium Purification System.
ANL Neg. No. 103-L5427.

Figure 2 is a more detailed schematic diagram of the sampling system connected to the purification system. Sodium is supplied to the sampling system from either the inlet or the outlet of the cold trap and returns to the purification system downstream of the trap. Samples are normally taken from the inlet side of the trap, and flow is maintained in the sampling system by the pressure differential across the cold trap. A small electromagnetic pump provides flow when sampling from the outlet side of the cold trap and can also be used to boost the flow rate when sampling from the inlet side. Normal flow rate through sample lines with the pump off is approximately 0.3 gpm. The pump can boost flow rates to as high as 1.5 gpm.

Sample flow is directed through either of the two samplers by operation of manual valves. The manual valves in the lead-shielded sampling cubicle are operated with flexible shafts. System isolation is provided by three pneumatic, fail-closed valves located near the juncture of sampling

and purification lines. All valves are bellows-sealed and have Inconel-asbestos secondary packings. Valve-bonnet leak detectors are interlocked with the pneumatic valves, the preheat system, and the sampling pump to shut down and isolate the system if a bellows fails. The pneumatic isolation valves are installed so that their bellows are isolated from the purification system when the valves are closed.

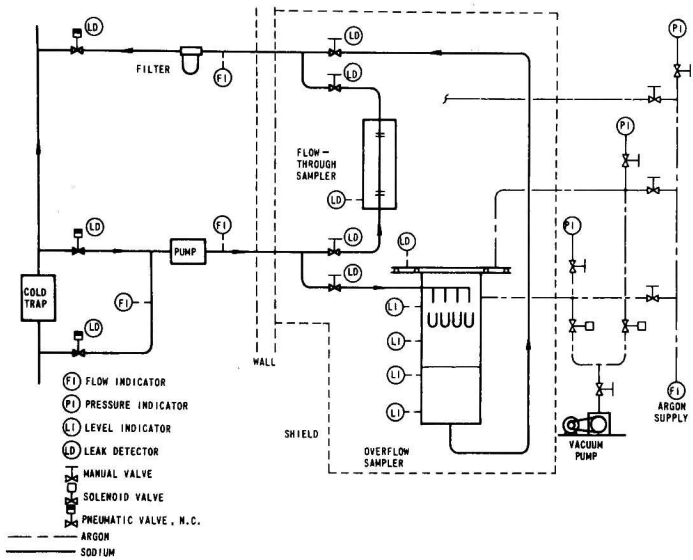

Fig. 2. Sampling System Connected to Primary-sodium Purification System. ANL Neg. No. 103-L5426.

The flow-through sampler is simply a removable vertical section of line with Swagelok tube fittings so various sample vessels may be installed directly in-line. The flow-through vessels are heated by a clam-shell oven. A leak detector in the bottom of the oven is interlocked to shut down and isolate the sampling system if the sample vessel or fittings leak.

The overflow sampler consists of an argon-atmosphere chamber with four sodium-inlet spigots. Four 10-ml beakers, supported on a rack below the spigots, are filled simultaneously. The beakers are flushed by allowing sodium to overflow to a reservoir, from which the sodium is returned to the purification system through a filter. Sodium level in the reservoir is monitored with electrical-contact level indicators and controlled by varying the argon pressure. The lid on the overflow sampler is sealed by two silicone rubber O-rings. The high-level probe and the leak detector between the O-rings of the lid are interlocked to shut down and isolate the sampling system in the event of high sodium level in the chamber or sodium leakage past the inner O-ring.

An argon/vacuum system is connected to the sampling chamber as shown in Fig. 2. Following installation of sample cups, the chamber is first evacuated and then filled with argon. During operation, the sodium level is raised or lowered by decreasing or increasing the argon pressure in the chamber. The leak-detection annulus in the lid seal is maintained under vacuum during sampling operations. Argon is also used to purge flow-through sample vessels during their installation.

Figure 3 is a schematic diagram of the FERD loop and its sampling system. Sodium is supplied to the delayed-neutron detector from the discharge of the intermediate heat exchanger (IHX), and returns to the primary tank below the sodium surface. To prevent syphoning of sodium from the tank in the event of a leak, the entire loop external to the primary tank is higher than the sodium level in the tank. There are two small tanks at which vacuum or argon pressure may be applied to fill or drain sodium from the loop. Circulation, provided by an electromagnetic pump, is normally constant at 100 gpm.

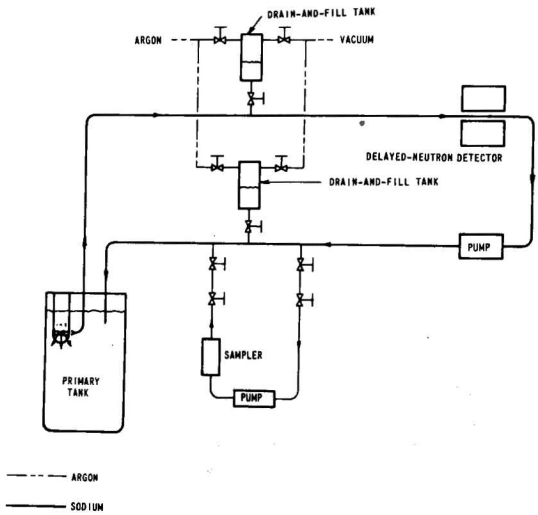

Fig. 3. FERD Loop. ANL Neg. No. 103-L5428 Rev. 1.

The sampling system and a plugging indicator were added to the FERD loop in 1967. These were used in 1968 to monitor quality of the primary sodium while the cold trap was being replaced and the sampling system of the primary-sodium purification system was being rebuilt. The plugging indicator was subsequently removed, and the sampling system has been in standby service since the purification system was returned to service in November 1968.

Figure 4 is a more detailed schematic diagram of the sampling system connected to the FERD loop. Sodium flow is induced with a small electromagnetic pump. The flow indicator is not calibrated, but maximum flow is estimated to be ~1 gpm.

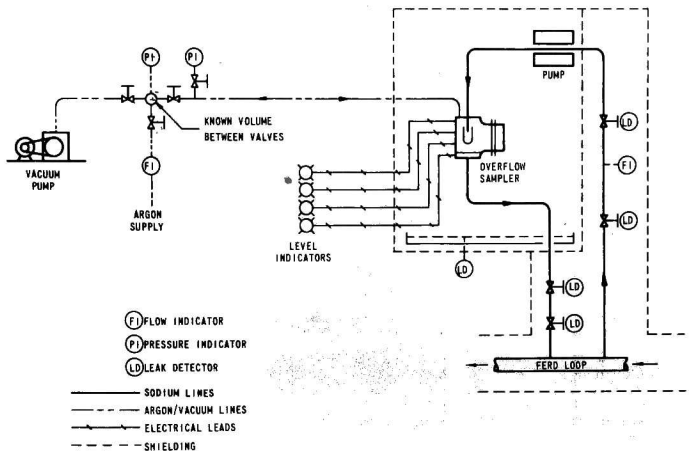

Fig. 4. FERD-loop Sampler. ANL Neg. No. 103-L5431 Rev. 1.

The sampler is essentially the same as the overflow sampler of the purification system, but is much smaller. The sample chamber consists of a 2-in. pipe tee modified to accommodate (1) an inlet-sodium spigot, (2) an outlet-sodium line, (3) an argon/vacuum line, and (4) level detectors. The sample beaker is inserted and removed through the branch of the tee. A metal O-ring (Temperature Compensating Coupling, made by DSD Company) seals the access port.

Because of the small volume of the sampler, level control is more critical than for the sampler of the purification system. The argon/vacuum system is arranged so that gas may be metered into and out of the sampler through a chamber of known volume.

Leak detectors in the bonnets of all valves and on the floor of the sampling cubicle are connected to audible and visual annunciators. In the event of a leak, the system is manually isolated and shut down.

B. System for Sampling Secondary Sodium

Figure 5 is a schematic diagram of the secondary-sodium purification system and its sampling loop. Sodium overflows from the surge tank to a recirculation section of the storage tank. It is pumped back to the surge tank by one of two electromagnetic pumps; the second pump is in

standby in case of failure on the on-line pump. A side stream from the recirculating loop is processed by the cold trap. A plugging indicator in parallel with the cold-trap monitors the sodium-oxide plugging temperature.

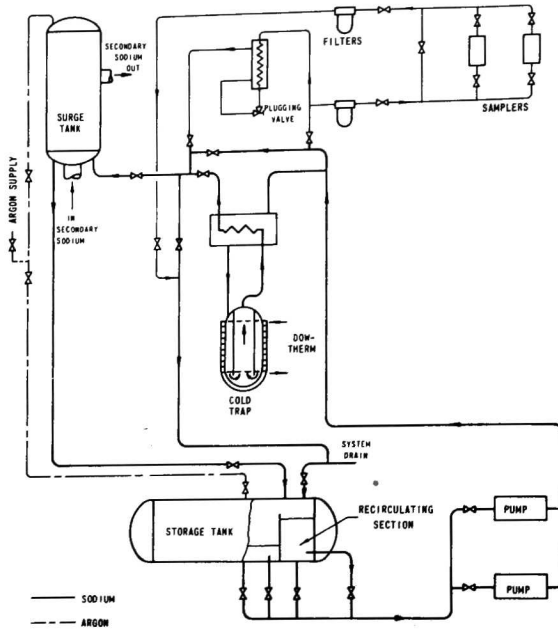

Fig. 5. Secondary-sodium Purification System.
ANL Neg. No. 103-L5432.

Figure 6 is a more detailed schematic diagram of the secondary-sodium sampling system. Sodium is supplied to the system from the inlet of the plugging indicator and returns to the purification drain line. Flow is maintained by the differential pressure between the inlet of the plugging indicator and the storage tank. Normal sampling flow rate is approximately 0.5 gpm.

By manipulation of manual valves, sodium is directed through either of two samplers or through a bypass. The flow-through sampler is essentially the same as that in the sampling system of the primary-sodium purification system. The overflow sampler is a small chamber in which a single 10-ml beaker may be filled. The chamber lid is sealed with a metal O-ring. Argon is supplied to the chamber through a sodium freeze trap. No level detection is provided.

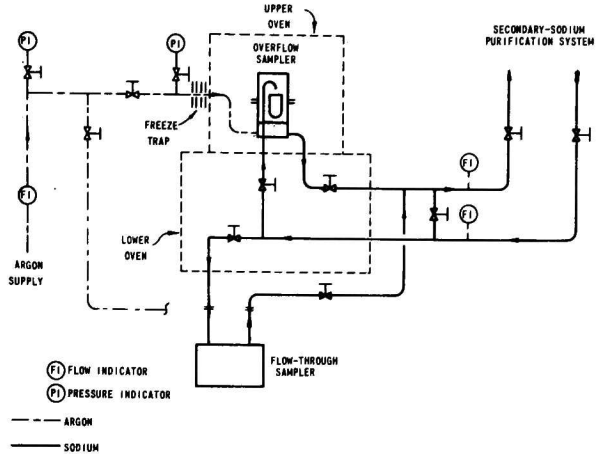

Fig. 6. Secondary-sodium Sampling System.
ANL Neg. No. 103-L5429 Rev. 1.

III. ROUTINE EBR-II SAMPLING PROCEDURES

Samples are taken routinely from the EBR-II primary- and secondary-sodium systems and analyzed for radionuclides, trace metals, oxygen, carbon, and hydrogen. Samples have also been analyzed for uranium, silicon, chloride, sulfide, cyanide, and nitride, although not on a routine basis. Archive samples (50-100 g in size) have been taken in aluminum tubes by both the overflow and the flow-through methods, and (10 g in size) in nickel-foil cups by the overflow method. Currently, primary-sodium archive samples are taken in nickel-foil cups weekly, and secondary-sodium archive samples are taken in aluminum tubes monthly.

Table II summarizes the sampling and analytical methods used at EBR-II.

TABLE II. Sampling and Analytical Methods Used at EBR-II

Impurity	Sample Vessel	Sampling Method	Sample Size, g	Analytical Method[a]	Comments
Radionuclides	Pyrex beaker	Overflow	10	γ-spectrometer	Total sample analyzed
Trace metals (volatile)	Quartz beaker	Overflow	10	Solvent extraction, atomic absorption	Total sample analyzed
Trace metals (nonvolatile)	Tritanium or tantalum crucible[b]	Overflow	50	Vacuum distillation, atomic absorption	Total sample analyzed
Carbon	Stainless steel extrusion vessel[c]	Flow-through	15	Oxyacidic flux	Analysis on three to five aliquots of ~1 g each
Oxygen	Stainless steel extrusion vessel[c]	Flow-through	15	Mercury amalgamation	Analysis on three to five aliquots of ~1 g each
Hydrogen	Stainless steel or nickel tube	Flow-through	20	Amalgam reflux[d]	Sectioned and extruded for analysis

[a]Analytical methods used are described in Ref. 2.
[b]See Fig. 8.
[c]See Fig. 7.
[d]Analysis performed at WADCO, Richland, Washington.

Samples for radionuclide analysis are taken in 10-ml Pyrex beakers. The total sample is dissolved, and an aliquot of the solution is counted with a gamma spectrometer.

Samples for trace metals that codistill with sodium (e.g., cadmium and zinc) are taken in 10-ml quartz beakers, and the metals of interest are separated from the sodium by solvent extraction. Samples for trace metals that do not codistill with sodium are taken in 10- or 50-ml tantalum or titanium crucibles, and sodium is separated from the metals of interest by vacuum distillation. In both cases, metal concentrations are measured by atomic-absorption spectrophotometry.

Samples for oxygen and carbon are taken in the extrusion vessels illustrated in Fig. 7. Ends of the sample that have been exposed to the atmosphere are discarded, and analysis is made on extrusion aliquots from the main body of the sample. Oxygen is determined by the mercury-amalgamation method, and carbon by the oxyacidic-flux method.

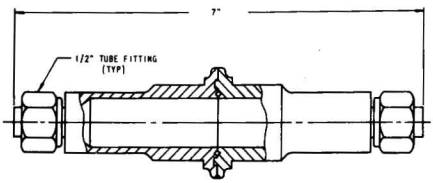

Fig. 7. Extrusion Vessels for Taking Sodium Samples for Analysis of Oxygen and Carbon. ANL Neg. No. 103-L5433.

Samples for hydrogen analysis are taken in 1/2-in. tubing. Sections for analysis are cut from the middle of the tube, and the ends exposed to the atmosphere are discarded. Both the isotope-dilution and the amalgam-reflux methods have been used to determine hydrogen concentration.* The amalgam-reflux method is currently used.

Sampling procedures are essentially the same, regardless of the system being sampled. However, the manipulations involved in the operation of individual systems are different because of the physical differences in the sampling systems. Sampling of primary sodium involves one additional hazard over that of sampling secondary sodium: intense gamma-radiation from ^{24}Na.

Five general steps are involved in sampling, as discussed below. These steps are: (1) preparation of sample vessel; (2) startup of sampling system; (3) sampling; (4) shutdown of sampling system; and (5) handling of samples.

*Analyses by isotope dilution are performed at Argonne-Illinois; analyses by amalgam reflux are performed at WADCO, Richland, Washington.

A. Preparation of Sample Vessel

Beakers used for radionuclides are rinsed with acetone and dried. Beakers used for trace metals are rinsed with aqua regia and demineralized water and dried. All beakers are stored in plastic containers until they are used. In preparation for sampling, the beakers are removed from their storage containers and positioned in the overflow sampler of one of the sampling systems. The sampling chamber is sealed, and an argon atmosphere is established.

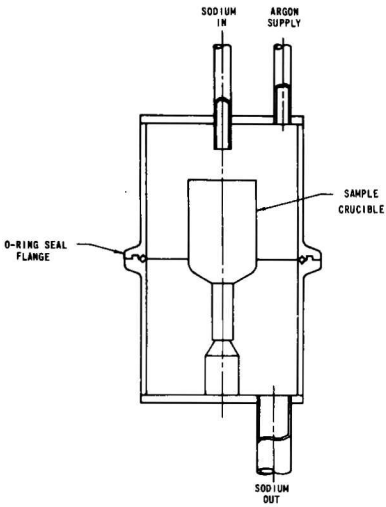

Fig. 8. Sampling Chamber for Taking Vacuum-distillation Samples. ANL Neg. No. 103-L5425 Rev. 1.

Titanium and tantalum crucibles are rinsed with hydrofluoric acid, aqua regia, and demineralized water and dried. A crucible is sealed into a sampling chamber as shown in Fig. 8. The chamber is filled with argon and then installed in one of the flow-through samplers.

Figure 9 shows an alternate method of filling these crucibles in the primary-sodium system. After being cleaned, the crucible is sealed into a transport chamber as shown in Fig. 9b. The chamber is then mated to the primary-sodium overflow sampler in place of the lid of the sampler. The vacuum-type gate valve is opened, and the crucible is lowered into the sampling position shown in Fig. 9a.

Extrusion vessels used in sampling for carbon and oxygen are washed with ethyl alcohol and water to remove residual sodium from the previous sample. Two vessels are then sealed back-to-back as shown in Fig. 7. The paired vessels are rinsed with acetone and dried. They are filled with argon and installed in one of the flow-through samplers.

Tubing used in sampling for hydrogen analysis is rinsed with acetone and dried. The tube is filled with argon and installed in one of the flow-through samplers.

Aluminum tubes used in taking archive samples are anodized in a 5% ammonium citrate-5% citric

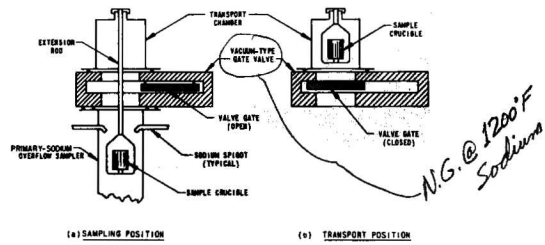

Fig. 9. Arrangement for Taking Vacuum-distillation Samples. ANL Neg. No. 103-P5424 Rev. 1.

acid solution, then rinsed with water and acetone and dried. They are filled with argon and installed in one of the flow-through samplers. Nickel cups used in taking archive samples are formed from 0.001-in. foil to fit inside a 10-ml beaker. The beakers, with the cups inside, are installed in one of the overflow samplers.

B. Startup of Sampling System

After the sample vessel is installed, the system must be heated above the melting temperature of sodium before a sample can be taken. The system is heated progressively from solid/liquid and solid/gas interfaces toward control valves. For example, the sampling system of the primary-sodium purification system is heated progressively from the connection with the purification piping and from the argon-filled samplers toward the manual control valves. Expansion of sodium as it melts is thus absorbed by the liquid sodium in the purification system and the argon gas in the samplers. The entire system is heated to a minimum temperature of 300°F before flow is established.

C. Sampling

After heat-up, flow is established through the sampler. With overflow samplers, the argon pressure is adjusted to match the sodium pressure, and then both the inlet and outlet sodium valves are opened. With flow-through samplers, the outlet valve is opened first to relieve pressure to the outlet sodium line, and then the inlet valve is opened. Flow is maintained for a minimum of 15 min. This ensures several volume changes in the sampling system and several hundred volume changes in the sample vessel. Flow may be maintained for longer periods if desired.

D. Shutdown of Sampling System

After the sodium flow has been maintained for the desired length of time, the flow is stopped by closing appropriate valves. With flow-through sampling, in which flow is upward through the sample vessel, the inlet valve is closed, and the sample is frozen while the sodium in the outlet line is molten and open to system pressure. This is done to limit the volume of the voids in the sample, which form because of shrinkage during freezing. Once the sample is frozen, the outlet valve is closed, and all heaters are deenergized.

With overflow sampling, the inlet valve is closed, and the sodium level is lowered in the sampling chamber. After the desired sodium level has been established, the outlet sodium valve is closed, and all heaters are deenergized.

E. Handling of Samples

Samples of secondary sodium may be removed from the samplers as soon as the sodium is frozen. Samples of primary sodium are usually left in the samplers for a minimum of five days to allow ^{24}Na to decay. Samples of primary sodium in 10-ml beakers have been removed with only one half-life (15 hr) decay of ^{24}Na and analyzed for short-lived radioisotopes. Small lead casks are used for transporting these samples; to eliminate the ^{24}Na activity, the sodium is separated from the isotopes of interest in the laboratory.

No precautions are taken to prevent atmospheric contamination of 10-ml samples taken by the overflow method. The sample chamber is vented to the atmosphere, and the lid is removed after the sampling system is frozen. Samples are taken from the sampling chamber and placed in plastic containers for transport to the laboratory.

Flow-through samples (in extrusion vessels and tubing) are removed from the system by disconnecting the tube fittings. These samples are capped and transported to the laboratory. Ends that had been exposed to the atmosphere are not used in the analysis.

Chambers containing a crucible (see Figs. 8 and 9) are disconnected from the sampling system and transported to the laboratory. The chamber is opened in an inert-atmosphere glovebox, and the crucible is transferred to a vacuum-distillation rig. Special care is taken to limit oxidation of these samples. Excessive oxide interferes with distillation and subsequent analysis for trace metals.

Archive samples in aluminum tubes are removed from the sampling system, capped, and stored. Archive samples in nickel cups are removed from the sampling system and stored in plastic containers holding an argon atmosphere. Lids are sealed on the containers with paraffin.

IV. ANALYTICAL RESULTS

Results of analysis of EBR-II sodium have been reported regularly in the monthly ANL Reactor Development Program Progress Reports since March 1967. Information concerning impurities is summarized here. All values given are typical unless otherwise noted.

A. Radionuclides

Table III lists the principal radionuclides in EBR-II sodium with sufficiently long half-lives to be measured routinely. Sodium-22 and ^{24}Na are activation products from ^{23}Na. Cesium-137 is a fission product

introduced into the sodium in 1967 from a fuel-cladding failure. Iodine-131 is a fission product from tramp uranium in the core region of the reactor. Increased levels of ^{131}I would be expected following cladding failures resulting in expulsion of bond sodium from the fuel element.

TABLE III. Principal Radionuclides in EBR-II Sodium

Isotope	Activity, μCi/g	Remarks
	Primary Sodium	
^{24}Na	1400	Saturation at 62.5 MWt; varies with power history
^{22}Na	5.0×10^{-2}	Increases with MWd of reactor operation
^{137}Cs	1.2×10^{-2}	Introduced in 6/67 by fuel-cladding failure
^{131}I	3.0×10^{-4}	Maximum with no fuel-cladding defects in reactor
	7.0×10^{-4}	Maximum to date with known fuel-cladding defects in reactor
	Secondary Sodium	
^{24}Na	4.0×10^{-2}	Saturation at 62.5 MWt

Sodium-24 is also present at low levels in secondary sodium (see Table III); this indicates that there is a small neutron flux on the IHX.

Tritium is present in primary sodium, secondary sodium, and several other plant systems, as shown in Table IV. Data compiled from analysis of sodium during cold-trap operation and during cold-trap outage indicate that much of the tritium produced in the fuel deposits in the primary cold trap. The tritium produced in fission is estimated to be distributed as follows:

1) 30% retained in the fuel.
2) 65% retained in the primary cold trap.
3) 3.5% retained in the primary sodium.
4) 1% retained in the secondary sodium.
5) <1% lost through the steam system.

This estimate is based on tritium analysis in primary and secondary sodium with and without cold-trap operation, on tritium analysis of four fissium-fuel samples, and on the assumption that EBR-II tritium yield is the same as the

thermal-fission yield. Figure 10 illustrates the effect of cold-trap operation on the tritium concentration in primary sodium.

TABLE IV. Tritium in EBR-II Plant Systems

System	Tritium, pCi/cm^3
Primary sodium	4.4×10^4
Secondary sodium	1.1×10^4
Primary argon	45
Secondary argon	7.5
Turbine condensate	72
Steam-drum blowdown	65
Steam condensed from line entering power plant	140
Steam-trap waste from superheaters	20
Shield-cooling air	1.3×10^{-2}

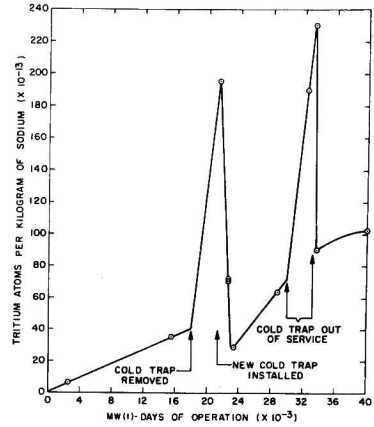

Fig. 10. Tritium in EBR-II Primary Sodium. ANL Neg. No. 103-P5193 Rev. 1.

Other fission and activation products have been detected in the primary sodium by counting the distillation residue from 50 g of sodium with a Ge-Li detector. Table V lists the activities of these radioisotopes in the primary sodium.

TABLE V. Activation Products in Primary Sodium

Isotope	Activity, μCi/g
^{110m}Ag	5.9×10^{-4}
^{54}Mn	5.2×10^{-5}
^{125}Sb	7.5×10^{-4}
^{117m}Sn	4.4×10^{-3}
^{113}Sn-^{113m}In	5.6×10^{-3}

B. Metals

Table VI lists typical results of analysis for trace metals in EBR-II sodium. All metals are determined by atomic-absorption spectrophotometry. Cadmium and zinc are separated from sodium chemically, the rest by vacuum distillation.

TABLE VI. Trace Metals in EBR-II Sodium

Metal	Concentration, ppm		Metal	Concentration, ppm		Metal	Concentration, ppm	
	Primary Sodium	Secondary Sodium		Primary Sodium	Secondary Sodium		Primary Sodium	Secondary Sodium
Ag	0.04	0.01	Cr	<0.02	0.01-0.5	Mo	<0.07	<0.07
Al	<0.06	<0.06	Cu	<0.02	<0.02	Ni	<0.04	0.01-0.2
Bi	2.0	<0.1	Fe	0.1-1.0	0.1-1.0	Pb	10.0	0.6
Ca	<0.02	<0.02	In	<0.06	<0.06	Sn	20.0	<0.3
Cd	0.08	<0.02	Mg	<0.005	0.005-0.05	Zn	<0.06	<0.06
Co	<0.02	<0.02	Mn	<0.005	0.005-0.05			

The source of lead in primary sodium is unknown. Analysis of archive samples indicates that lead has been present since the system was filled in 1963. Tin and bismuth came from an apparent spill of tin-bismuth eutectic alloy (42% tin, 58% bismuth) from the shield-plug seals in July 1965. Copper, though currently below detection limits, caused plugging problems in the primary plugging indicator in 1967 (see Sec. I).

Figure 11 illustrates the history of tin, bismuth, and copper in the primary sodium since 1965. Tin has remained at a level of approximately 20 ppm

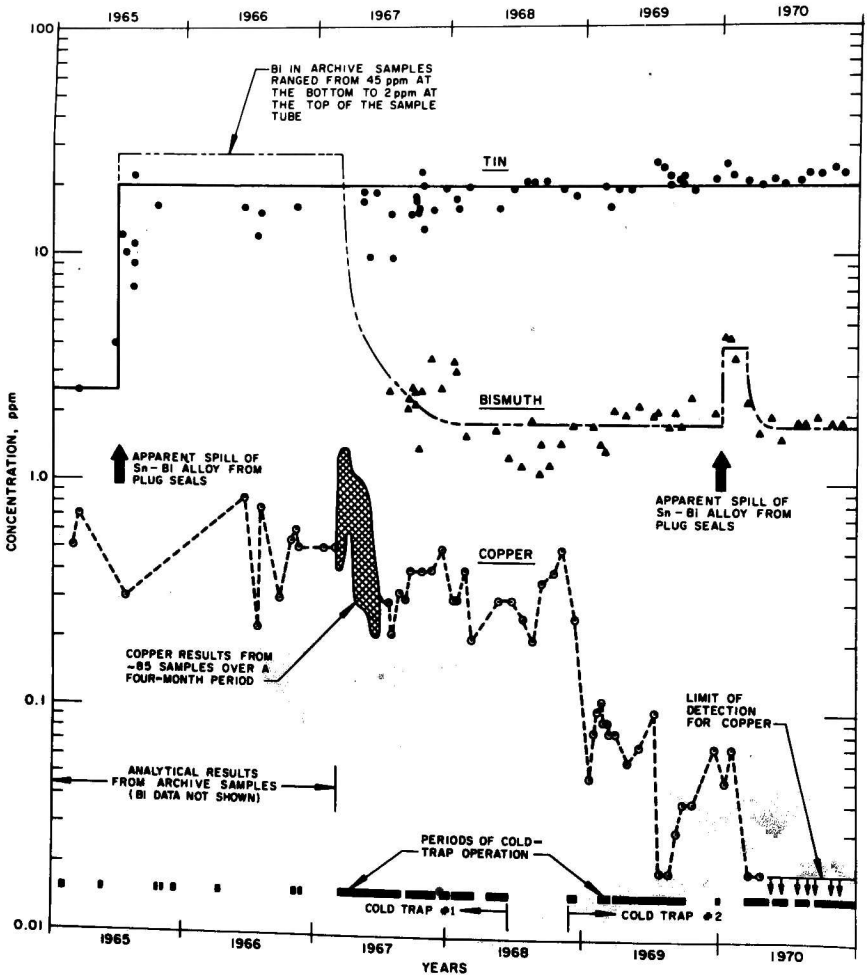

Fig. 11. History of Tin, Bismuth, and Copper in EBR-II Primary Sodium. ANL Neg. No. 103-P5425.

since it was introduced in 1965. Bismuth was reduced to approximately 2 ppm with extended cold-trap operation starting in 1967. Data for bismuth prior to 1967 are not shown in Fig. 11, because the analytical results on archive samples had a wide scatter. The results varied from 45 ppm at the bottom of these samples to 2 ppm at the top. Bismuth apparently precipitated to the bottom of the sample tube as it solidified. The pre-1967 history of bismuth that is shown in Fig. 11 was estimated from the tin data and the cold-trap operating history. The bismuth concentration following the spill of tin-bismuth eutectic alloy in July 1965 should have been 58/42 of the tin concentration. The bismuth concentration probably remained at that level (~27 ppm) until the cold trap was operated extensively beginning in March 1967. A second introduction of a small amount of seal alloy to the sodium apparently occurred in January 1970. During that period, while the cold trap was not in operation, the bismuth concentration rose to 4 ppm. The cold trap rapidly reduced the bismuth to 2 ppm again in March 1970.

The principal source of copper in primary sodium was unclad bus bars that supplied current to the emergency reactor-coolant pump. These bus bars were clad with stainless steel in 1967, after the copper plugs were discovered in the plugging-indicator system. Extended operation of the cold trap reduced the copper concentration from 0.5-1.5 to about 0.2-0.5 ppm in about four months. Further reduction did not occur until a new cold trap replaced the old one in 1969. However, the replacement may be coincidental to the copper behavior. Possibly, most of the copper (~20 lb) that dissolved from the bus bars from 1963 to 1967 precipitated within the primary tank. With extended cold-trap operation beginning in 1967, the copper slowly redissolved and deposited in the cold trap. The supply of copper may have eventually been depleted, and the concentration in sodium dropped below detection limits.

C. Nonmetals

Table VII lists results of analysis for nonmetallic impurities in sodium. Because of the large inventory of sodium (86,000 gal in the primary system and 13,000 gal in the secondary system) and the policy (since 1967) of operating the cold traps as much as possible, little or no variation is seen in nonmetal concentrations.

TABLE VII. Nonmetals in EBR-II Sodium

Constituent	Concentration, ppm		Constituent	Concentration, ppm	
	Primary Sodium	Secondary Sodium		Primary Sodium	Secondary Sodium
Carbon	<2.0	<2.0	Nitride	~0.2	<0.1
Chloride	<5.0	<5.0	Oxygen	<2.0	<2.0
Cyanide	<0.2	<0.2	Sulfide	<2.0	<0.2
Hydrogen	<0.1	<0.1			

V. FUTURE PLANS

Two recent publications[2,3] prescribe methods and specifications for sampling and analyzing sodium. Experience at EBR-II weighed heavily in the selection of sampling and analytical methods[2] and in prescribing purity specifications.[3] Every effort will be made in the future to conform to these methods and specifications and to provide input for updating them as advances are made in the state of the art.

The number of impurities monitored on a routine basis will be expanded to include nitride, boron, silicon, and alpha emitters. A tentative sampling schedule for FY 1972 is listed in Table VIII. The schedule for sampling primary sodium is very rigorous and represents maximum utilization of existing sampling equipment.

TABLE VIII. Tentative Schedule for Analysis of EBR-II Sodium in FY 1972

Analysis	Method	Frequency
	Primary Sodium	
Oxygen	Plugging indicator	Daily
Oxygen	Amalgamation	Monthly
Carbon	Dry oxidation	Monthly
Hydrogen	Amalgam reflux	Monthly
Nitride nitrogen	Micro-Kjeldahl	Quarterly
Metallic impurities	Atomic-absorption spectrophotometry on distillation residue	Monthly
Cadmium and zinc	Atomic-absorption spectrophotometry on solvent extracts	Quarterly
Boron and silicon	Colorimetry	Monthly
^{131}I	Gamma-ray spectrometry on solvent extracts	Weekly
^{137}Cs and ^{22}Na	Gamma-ray spectrometry on solution of bulk-sodium sample	Weekly
Other activation and fission products	Gamma-ray spectrometry on distillation residue	Monthly
Tritium	Liquid-scintillation counting	Monthly
Alpha emitters	Alpha-counting	Bimonthly
Historical; 10-g sample	-	Weekly
	Secondary Sodium	
Oxygen	Plugging indicator	Daily
Oxygen	Amalgamation	Monthly
Carbon	Dry oxidation	Monthly
Hydrogen	Amalgam reflux	Monthly
Nitride nitrogen	Micro-Kjeldahl	Quarterly
Metallic impurities	Atomic-absorption spectrophotometry on distillation residue	Monthly
Boron and silicon	Colorimetry	Monthly
Radioisotopes	Gamma-ray spectrometry on bulk-sodium sample	Monthly (during reactor operation)
Tritium	Liquid-scintillation counting	Monthly
Historical; 100-g sample	-	Monthly

Completion of the radioactive sodium chemistry loop (RSCL)[4] in early 1971 has provided a versatile facility for testing and operating on-line monitors and other sodium-purity monitoring equipment in EBR-II primary sodium. Immediate plans call for operation of oxygen, hydrogen, and carbon meters,[5] a specimen equilibration device,[5] an analytical cold trap,[6] and an in-line vacuum-distillation sampler[7] in the RSCL starting in FY 1972.

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